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Conformational Disorder and Ultrafast Exciton Relaxation Dynamics in PPV-family Conjugated Polymers

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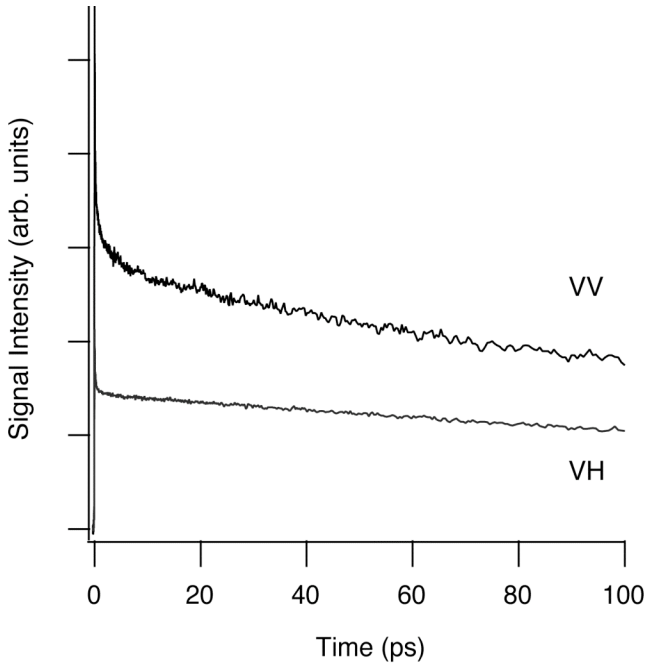

Figure S1. Pump-probe data for MEH-PPV in chlorobenzene solution. Transients for the VV and VH polarizations, collected simultaneously.

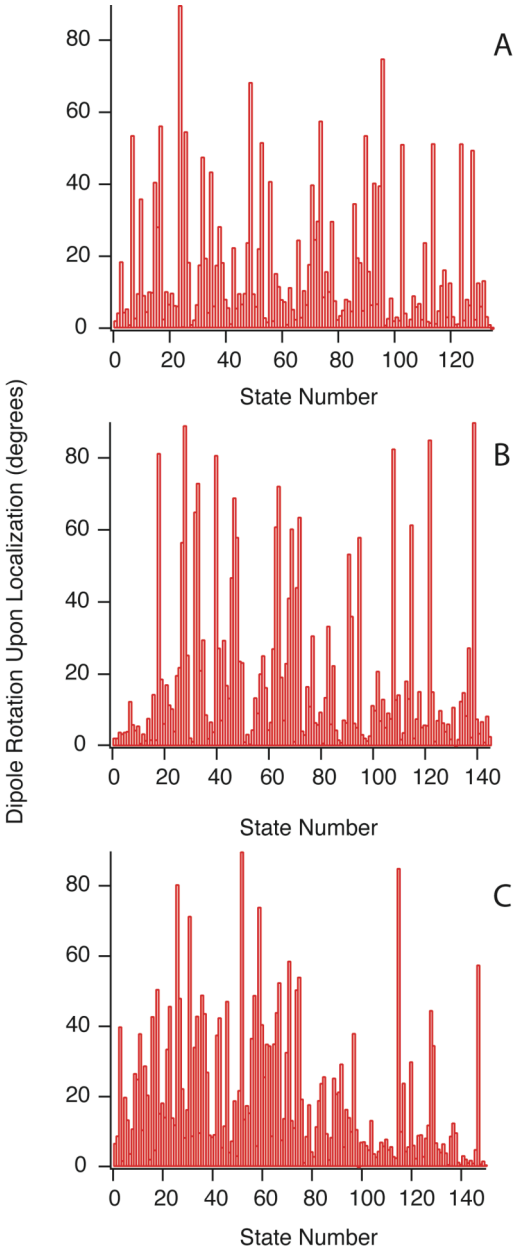

Figure S2. The rotation of the dipole moment upon localization for the 3 chains shown in figure 1. The majority of the dipoles are rotated by fewer than 10º upon localization. However, a few chromophores may be rotated by as many as 85–90º.

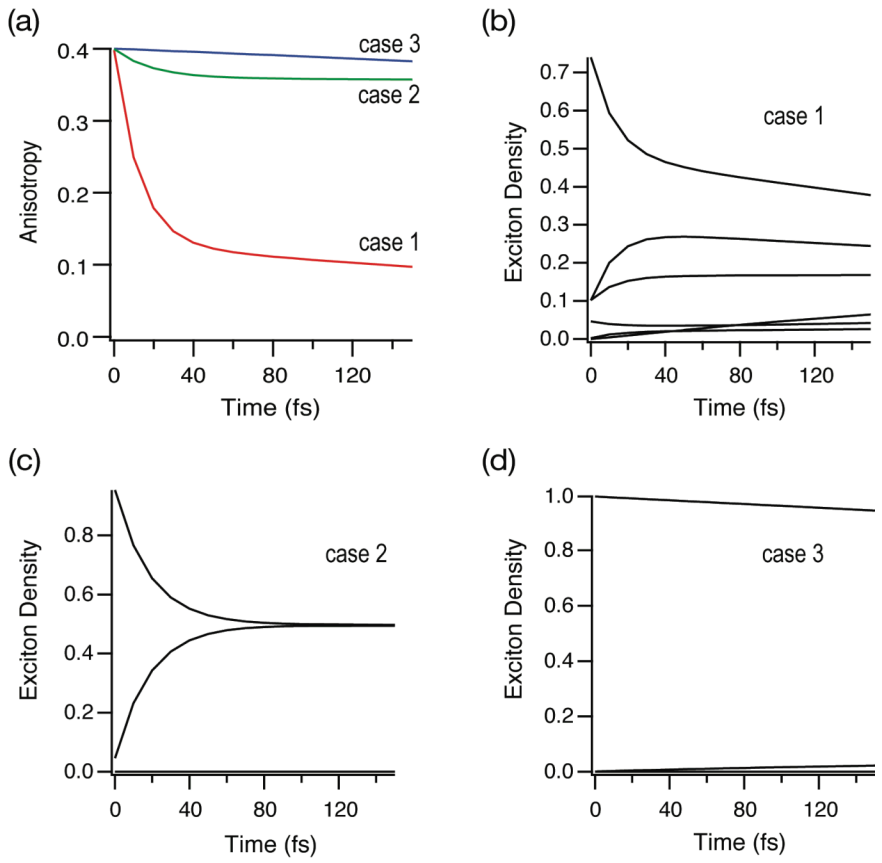

Figure S3. a) Anisotropy decays for chain C when only one state is initially excited. Each trace corresponds to one of the following cases: Case 1- Initially delocalized, strongly interacting exciton; Case 2- Interchain exciton; Case 3- Initially localized, weakly interacting exciton. b) The redistribution of exciton density (between sites) for the initially delocalized exciton. Each trace corresponds to a different site/conformational subunit, n, on the polymer chain. c) An interchain exciton. The two traces correspond to conformational subunits that couple through-space. d) An isolated state. This exciton is localized on one conformational subunit which is only weakly coupled to others. These neighbors are shown as slight increases in exciton density at the bottom of the plot.

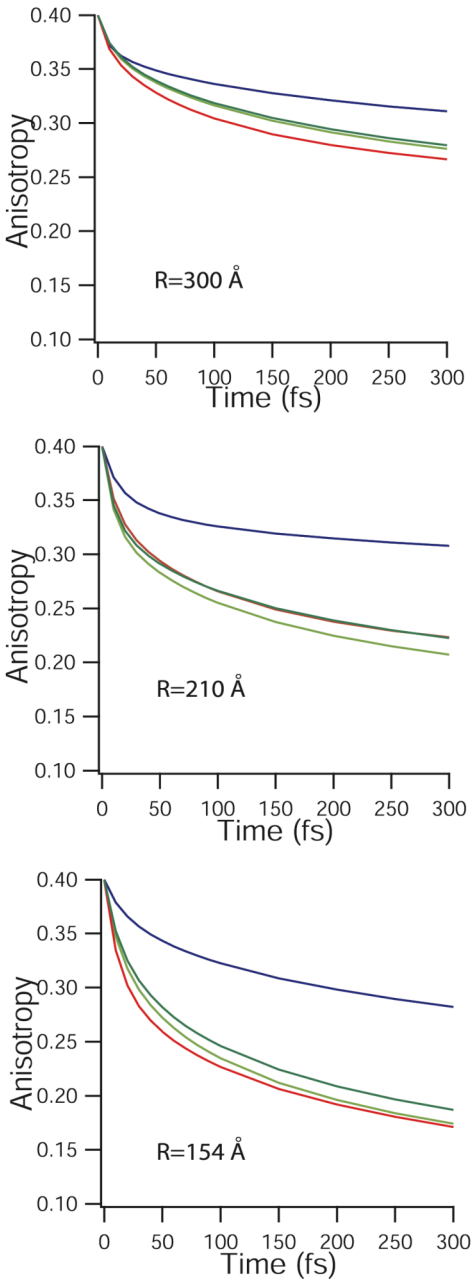

Figure S4. The simulated anisotropy decays for the three chains shown in figure 1. Each chain is excited at several wavelengths as shown. Blue lines correspond to excitation at 30000 cm^{-1} by a Gaussian pulse of 500 cm^{-1} fwhm; dark green is 28000 cm^{-1}; green is 27500 cm^{-1}; red is 26000 cm^{-1}. As the radius of gyration is decreased, the coupling between chromophores is increased owing to the smaller average separation between them. There is an associated more rapid decay in the anisotropy as the size is decreased. A systematic excitation wavelength dependence was difficult to establish in

single chains. When excitation is to the high energy side of the absorption peak, very few states are excited and those are often rather energetically different from other states, and the states are spaced further apart (see figure 6). We found there to be little overlap among these high lying states, so that the rate of transfer was estimated to be slow using the present simple model based on eq 11, cf. Figure 2. This results in very slow calculated anisotropy decay. Higher excited states and high frequency vibrations were not included in the simulations and would likely increase the rate of the anisotropy decay.

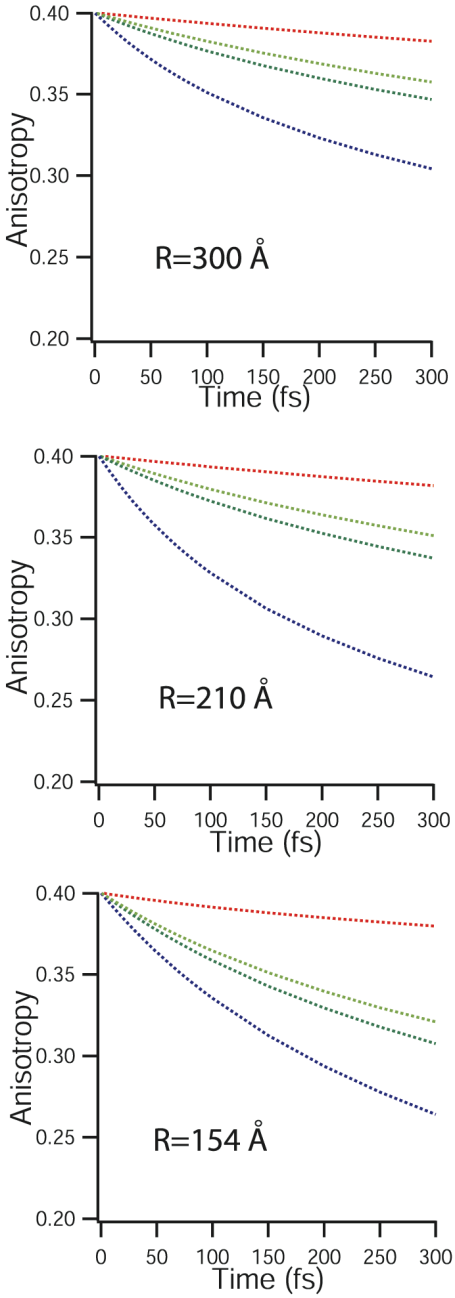

Figure S5. The simulated anisotropy decays for the three chains shown in figure 1. Each chain is excited at several wavelengths as described in figure S4. Here, the Förster model was used to calculate rates.